ANOMALOUSLY HIGH FLAMMABILITY OF LOW VOLATILITY FUELS
DUE TO ANOMALOUSLY LOW IGNITION TEMPERATURES.

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Fuel flammability is usually predicated on flash points, resulting from
exposure of fuel to flame. Low molecular weight (high volatility)
fuels have lower flash points and thus are judged more flammable than
low volatility fuels. A startling reversed relationship has been shown
to exist, however, for lower members of the alkane series, between
molecular weight and ignition temperature (IT), occasioned by contact
with hot surfaces: up to a point, less volatile higher molecular weight
fuels have lower IT's and are more easily ignited when exposed to hot
surfaces. For higher members of the alkane family this trend reverses,
resulting in minimum IT's for the C_5 - C_9 alkanes. Branched chain
alkanes, arenes and olefins also have anomalously high IT's. Free
radical effects are unimportant among factors influencing ignition
temperature; ionic effects may be important, as is the case for fires
involving active metal, phosphorus, thermite and similar inorganic
incendiary agents. This may be useful in fuel selection, if fires are
anticipated to result from contact with hot metal surfaces, as in
aircraft crashes, fuel spills on hot engine surfaces, or similar
effects, instead of by contact with flame. Molecular modelling
considerations will be discussed to explain the anomalous trends.

I. Ignition Temperatures (IT).

Ignition temperature is a poorly understood fuel characteristic which
has received little previous attention. This is despite the fact that
ignition temperature may arguably be the single most important fuel
characteristic in terms of catastrophic ignition by gunfire, aircraft
crashes, fuel spills on hot engine surfaces, and other instances of
obvious military (and commercial) aviation interest. From the
standpoint of fire prevention, and in particular design of practical
jet fuels capable of resisting ignition from such effects while
fulfilling normal operational combustion performance requirements, it
is suggested that IT's should be given an in depth examination.

Fuel ignition can be initiated by either of two effects: contact of the
fuel with a flame, or with a hot surface. For ignition by flame
contact, the important fuel characteristic is the flash point (FP); for
ignition from a hot surface, ignition temperature is important.

Flash points are routinely measured by heating a sample of the liquid
in either a closed or open cup assembly, with a small flame continually
passed over the surface of the liquid. The flash point is the lowest
temperature at which the fuel vapors ignite with propagation of the
flame beyond the source of ignition. Since it is principally a measure
of fuel volatility, flash point is most associated with the molecular
weight of the fuel component within a given chemical family.

IT measurements are not as precise. Typically, fuel is directed onto a
hot surface at a given temperature, and allowed to heat for up to ten
minutes. (1) The IT is the lowest temperature at which a flame occurs
(in some cases, exothermic decompositions not necessarily accompanied
by a flame). Often the flammable liquid will decompose to other

materials during the heating period. Thus, ignition temperature may
not really be a characteristic of the original material, but rather of
its decomposition products. In addition to rate and duration of
heating, other variables also affect IT measurements: shape and size of
the test chamber, air concentration, nature of the heated surface
(including catalytic effects), and temperature of the surface.
Therefore, IT measurements are frequently only poorly reproducible:
ignition temperature data for a compound, taken by different
individuals, can have very greatly differing values. (2)

II. Free Radical Fire Effects, and the Fire Tetrahedron. (3)

Until twenty years ago, there were three important requirements known
for a fire -- fuel, oxygen, and heat. These were commonly considered
as components of the "fire triangle", the removal of any one being
sufficient to extinguish a fire, and the presence of all three required
for fire initiation and propagation. As free radicals became more
understood, the "fire triangle" was expanded to the "fire tetrahedron".

Free radicals are non-ionic high energy intermediates which form easily
in high temperature reactions. Fire growth involves an avalanching
oxidative propagation of free radicals in vaporized fuel-air mixtures:
one free radical creates several others, and with descendent free
radicals forming in profusion in a continuing and proliferating
propagation throughout the fuel-air mixture.

Today, therefore, fires are characterized by the "fire tetrahedron"
(fuel, heat, air, and the presence of propagating free radicals).

For ignition of fuels by contact with flame, in which flash points have
most meaning, free radical events are entirely operational. In such
fires, the flame ignition source actually is a free radical plasma,
from which high energy free radicals are transferred to fuel vaporized
by heat of the flame. Situations which promote free radical formation
are conducive to ignition of the fuel under these conditions; and
agents such as the Halons which quench free radical formation are thus
optimum fire extinguishing agents for such fires.

III. Ionic Fire Effects: A Return to the Fire Triangle?

This discussion will attempt to point out that not all fires should be
characterized by the "fire tetrahedron". In fact, many fires of
military and commercial importance may best be characterized by the
"fire triangle", with free radicals being totally unimportant.

Thus, fires arising from ignition of magnesium, titanium, and other
active metals would best be described as involving ionic (not free
radical) effects in both initiation and growth of the fire.

$$e.g., \qquad Mg^{O} + 1/2\ O_2 \ ----->\ Mg^{++}\ O^{=} \qquad\qquad 1)$$

"Ionic fires" can perhaps best be differentiated from free radical
fires in terms of the ionic pathways and products of the ionic
reactions, with no role of free radical propagating intermediates. The
"flame" of an ionic fire is a plasma of incandescent ions, lacking in
free radical components.

Phosphorus, thermite and other inorganic or pyrotechnic fires also
would appear to be ionic and not free radical in nature. For ignition

of other combustibles by active metal or other inorganic incendiaries, it is now suggested that the mode of such ignitions may be that of contact with a hot surface rather than by contact with a flame.

Along these lines, Halons which quench free radicals and thus prevent propagation of "free radical" types of fires are completely ineffective against active metal "ionic" types of fires.

IV. Possible Ionic Effects in Ignition Temperature Correlations.

For fires resulting from ignition by contact of the fuel with hot surfaces, this discussion will attempt to demonstrate that while free radicals are certainly formed due to energy transfer and resulting bond breakages, the initiating events are not free radical in nature. In actuality, those fuels which would appear to be most susceptible to free radical formation often are among the most resistant to ignition by contact with hot surfaces! Thus, olefins and alkyl-substituted benzenes are far more susceptible to free radical substitution than are alkanes, due to resonance stabilization of the resulting free radical intermediates. (4) On the other hand, when comparing olefins and arenes with alkanes of similar volatility, the olefins and arenes frequently have higher ignition temperatures. Branched chain alkanes also undergo free radical reactions more readily than straight chain alkanes, but have higher IT's; and cyclopentanes are more reactive to free radicals than are cyclohexanes, but again the cyclopentanes have higher IT's (4,5) Representative data is shown in Table I.

Table I. Ignition Temperatures (IT) and Boiling Points (BP), in $^{\circ}$F, for Alkanes, Olefins and Arenes. (2,6,7)

Alkane	BP	IT	Olefin	BP	IT	Arene	BP	IT
butane	31	826	1-butene	21	829			
methyl-cyclohexane	214	545				Toluene	232	1026
methyl-cyclopentane	161	624						
octane	257	428						
2,2,4-trimethyl-pentane	211	784						

In Figure 1, moreover, there is an anomalous decrease in ignition temperature of alkanes with increasing molecular weight, for the range of alkanes from methane (C_1) through octane (C_8). Precise data is not prevalent for the higher alkanes. As shown in the lower projected track of the IT values for the various alkanes, one possibility certainly lies in an asymptotic sweep along a 400° IT isotherm, for alkanes beyond C_8. An inescapable suspicion lurks here, however,that a possible thermal cracking may occur at this temperature if the hydrocarbon is permitted to linger at the heated surface for up to ten minutes, in accordance with the ASTM operating procedures for this determination. (1) Thus, alkanes larger than nonane could conceivably have higher ignition temperatures; but by undergoing slow pyrolysis at 400° F, some alkanes in the minimum IT region characeristic of $C_5 - C_9$

would form, with these igniting at this spuriously low temperature.

There is indeed some evidence for a possible increase in IT's for the higher alkanes; i.e., a minimum zone of IT's may exist for alkanes in the region of pentane through nonane ($C_5 \sim C_9$). This is shown in Figure 1 as the upper projected track for the alkanes beyond C_9. It is obvious that either track could actually pertain, and that currently available data is insufficient and good values are probably poorly available with existing equipment and technique.

If this mimimum zone for ignition temperatures indeed exists, the hexane through decane range of alkane would appear to represent the most dangerous species in jet fuel formulations: these alkanes have unsuitably low flash points and ignition temperatures. In terms of ignition from hot surfaces, these would be highly prone to enflame due to the low ingition temperatures, and then would promote uncontrollable proliferation of the fire because of the low flash points.

Experimental evidence is too sparce to fully support an ionic event for typical hot surface ignitions. However, it has previously been demonstrated that the nature of the hot surface can have significant effects on ignition temperatures. Thus, benzene exhibits quite higher ignition temperatures in iron containers than in quartz, and even higher in zinc. (2) As will be discussed below, this may be most consistent with the relative emissivities of these materials. However, silica (quartz) can be acidic; and ferric oxide is significantly more acidic than zinc oxide. Thus, there may be cationic catalysis provided by an acidic surface, which can serve to greatly favor bond ruptures in alkanes. (4) Cationic and emissivity effects may be of importance with regard to incorporation of metals or coatings for aircraft parts which may be anticipated to be most likely to come into contact with fuel leaks in combat gunfire or in controlled crash situations.

V. Surface Emissivity Effects.

Emissivity is the energy radiated from a unit area of a surface, in a unit of time. This is greatly dependent on the nature of the surface: for example, rough surfaces are more emissive than smooth surfaces. With regard to the decreasing ignition temperatures noted above, with zinc surfaces influencing a higher IT for benzene than iron, and quartz surfaces providing the coolest IT of all three, this is consistent with the relative trend of increasing emissivities: quartz is a more efficient heating surface than smooth unoxidized iron or zinc.

VI. Molecular Effects Which May Influence Ignition Temperatures.

Fuel component characteristics have been identified as having possible impact on the ignition temperatures are described below. None of these appear in any way to be associated with free radical effects.

1. Molecular weight, and speed and inertia effects.

Since the anomalous decrease of ignition temperatures with increasing molecular weight is observed only from methane through nonane, other effects in the alkanes must offset any role of molecular weight in reducing ignition temperatures. Molecular weights are inversely proportional to molecular velocities, however, as shown in Figure 2. Since the heavier molecules have lower velocities, there is an increased residence time for these in the vicinity of a hot surface,

with increased time for energy transfer to the molecule. Heavier molecules also have greater inertia and thus less ability to move away from a hot surface than would a lighter molecule.

2. Molecular rigidity.

This appears to be a very important effect, not only in the straight chain alkane family, but even more so for branched chain alkanes, cycloalkanes, olefins and aromatics. As stated previously, these species are particularly susceptible to free radical reaction systems; but surprisingly, these are frequently very considerably more stable than are the alkane analogs, with regard to ignition by fuel contact with hot surfaces. Examinations of molecular models reveal that, compared to the straight chain alkanes, all these other species are very considerably more rigid, with very considerably reduced rotational degrees of freedom within the molecular structures. This would then impart a pronounced decrease in "floppiness" of the molecule in its impact with a hot surface, allowing the more rigid structure to rebound readily and rapidly, with correspondingly considerably reduced residence times in the vicinity of the hot surface, and considerably reduced energy transfer from the surface to the fuel molecule.

This effect may be of importance in design of new fuel compositions: olefinic, branched chain, cyclic (napthenic) and aromatic moeities would impart higher ignition temperature characteristics.

3. Specific molecular heat.

For the smaller molecules, apparently, factors of relative speed and relative rigidity are overpoweringly important. Within the lower range of the alkanes, each addition of a methylene unit imparts a significant increase in molecular weight and in internal degrees of rotational freedom. In going from ethane to propane, for example, there is a 17% decrease in speed at 1000° F; whereas decane is only 5% slower than nonane at this temperature. Internal rotational degrees of freedom are even more considerably enhanced for propane, which is very flexible compared with ethane, which is remarkably rigid; but decane and nonane have very little difference in "mushiness" due to this effect. Thus, decreased speed and rigidity effects arising from increased molecular weight are very much less important for the higher alkanes.

Moreover, higher alkanes begin to enjoy the benefit of increased "molecular specific heat". When lower alkanes such as ethane or propane are energized by radiational heat, all atoms of the small molecule are fairly equally irradiated. For significantly larger molecules, some atoms will be in the shadow of others. The hotter surface atoms can then transfer some of their increased energies to the cooler internal atoms. Thus, a higher ignition temperature will be required to attain decomposition energies for a molecule large enough to provide shadowing by some of its atoms to other neighboring atoms.

Thus, the anomalous high ignition temperatures for higher alkanes seen in Figure 1 may actually represent valid IT's; and the lower points constituting the asymptotic sweep at the 400° isotherm for these higher alkanes may prove to be unrealistically low.

VII. Recommendations for an IT Differential Scanning Calorimeter.

If more realistic IT determinations had lower time requirements

(perhaps a second instead of ten minutes), IT values for fuel components would probably be considerably increased. Modification of a conventional differential scanning calorimeter (DSC) could provide a convenient and accurate determination. Minute samples of the fuel components could be periodically injected, at higher and higher temperatures, until a sudden exotherm signal is attained. The first derivative appearance of the IT point with this scheme may make for a more reproducible determination. Automatic injection devices, coupled with automatic temperature controlling, should provide rapid and easy injections with minimum attention requirements for the determination.)

VIII. Fuel Design for Fire Prevention.

It may be possible to design fuels meeting operational combustion requirements, (i.e., burning satisfactorily when ignited with a flame), at the same time providing maximum resistance to ignition on contact with a hot surface (as in aircraft crashes, leakage of fuel onto hot engine surfaces, and similar situations). From the foregoing preliminary considerations, attention could be given to elimination of alkane content in the region $C_5 - C_{10}$), since these components may be in the minimum zone of IT's and also suffer from unduly low flash points. This cut could be catalytically dehydrogenated to olefinic or aromatic stocks, or catalytically rearranged to branched chain isomers or cyclolalkane analogs. It could also be alkylated with isobutylene to provide higher molecular weight and branched chain character. All of these should result in higher ignition temperatures, lower vapor pressure, increased density, and decreased viscosity effects, which should prove desirable from the standpoint of fuel characteristics.

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Figure 1. Correlations of Ignition Temperatures and Flash Points for n-Alkane Components.

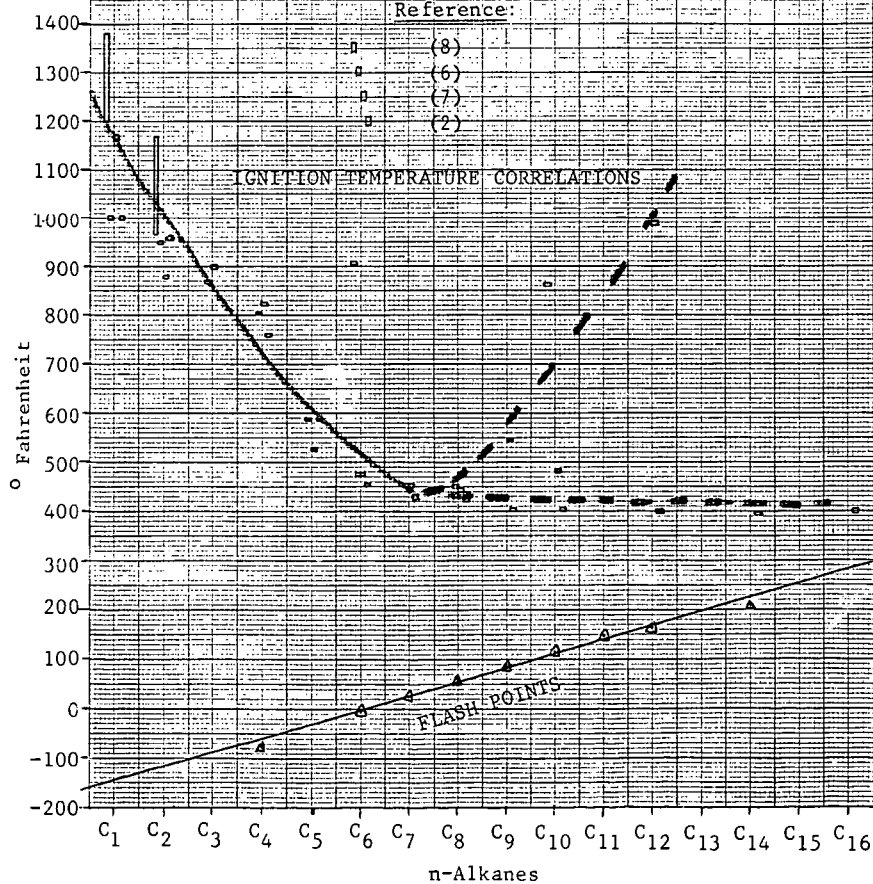Key to References for Relative Positions of Data Points

Reference:
(8)
(6)
(7)
(2)

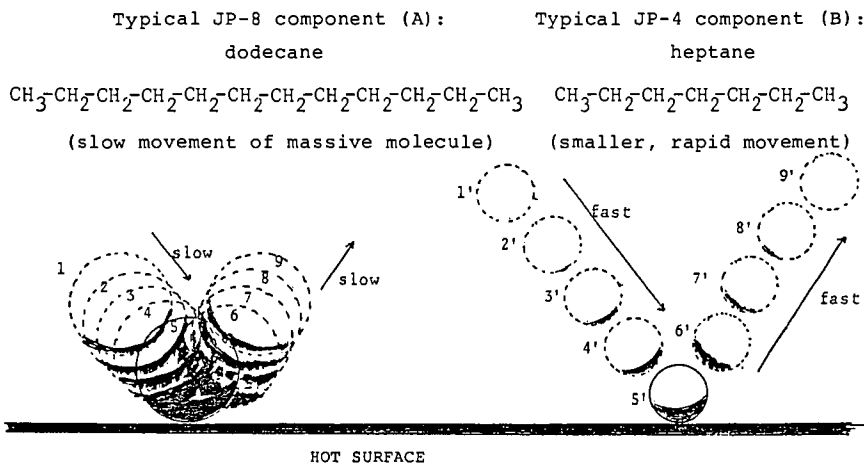IGNITION TEMPERATURE CORRELATIONS

FLASH POINTS

° Fahrenheit

n-Alkanes

Figure 2. Molecular Characteristics Affecting Ignition Temperatures.

Typical JP-8 component (A):   Typical JP-4 component (B):

dodecane   heptane

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$ $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

(slow movement of massive molecule)   (smaller, rapid movement)

HOT SURFACE

[(1), (2), (3) ... (8), (9) above indicate positions of molecules A and B at same time intervals, relative to hot surface area.]

Molecular velocity at temperature (T, ^{O}K) is inversely proportional to the molecular weight (M); smaller molecules have greater speed.

$$Average \ velocity = 14,600(T/M)^{\frac{1}{2}} \ cm/sec$$

The slow moving heavy molecule A (above) is therefore near the hot surface longer than the lighter and faster B, and A has more time available to absorb energy from the hot radiating surface.

The larger molecule A has more mobile C-C bonds and therefore more rotational degrees of freedom than the smaller B. Thus, A will tend to be "mushier" with less elastic recoil on impact with the hot surface than the smaller, more rigid B which can bounce away more readily. Again, molecule A will have more time to energize than B.

To offset this, and although the larger molecule has greater surface area enabling it to absorb more heat than the smaller molecule, the large molecule's volume is increased even more than is the surface area (by comparison with the smaller molecule). Absorbed heat is then dissipated more through the large molecule, which accordingly is cooler than the small molecule. This effect is more pronounced with increased molecular weights (and volumes).   In this case A (dodecane) needs more heat (with a higher ignition temperature) to energize it to its decomposition point than does B (octane). For smaller molecules (e.g., comparing hexane [C_6] and propane [C_3]), this offsetting factor of increased molecular specific heats is not as important as the molecular speed and rigidity effects: in such cases the heavier molecule has the lower ignition temperature.